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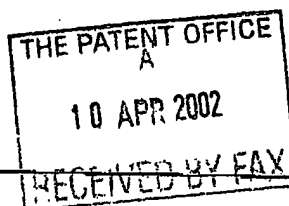
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P01/7700 0.00-0208263.4

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The Patent Office

Cardiff Road
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1. Your reference

MSP617

2. Patent application number

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10 APR 2002

0208263.4

3. Full name, address and postcode of the or of each applicant (underline all surnames)

DOW CORNING CORPORATION

Midland

Michigan 48611

USA

Po. Box 994

Intellectual Property

Col232

2200 W. Salzburg Road.

Midland

MI 48686-0994

Patents ADP number (if you know it)

414029003

If the applicant is a corporate body, give the country/state of its incorporation

USA/Michigan

08506040001

4. Title of the invention

PROTECTIVE COATING COMPOSITION

5. Name of your agent (if you have one)

A M Donlan

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

DOW CORNING LIMITED
Cardiff Road
Barry
CF63 2YL

Patents ADP number (if you know it)

07995244001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
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Yes

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

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See note (d))

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Patents Form 1/77

Patents Form 1/77

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Continuation sheets of this form

Description 7Claim(s) 1

Abstract

Drawing(s) 1

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Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

1 Fee Sheet

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

A M Donlan

10 April 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

A M Donlan 01446 723740

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PROTECTIVE COATING COMPOSITION

[0001] The present application describes a process for the preparation and/or coating of powdered particles using atmospheric pressure plasma techniques.

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[0002] The treatment of powders using atmospheric pressure plasma has been previously described. In JP 06-000365 there is provided an apparatus for continuously plasma treating a powder by coaxially pivoting a metallic inner and outer cylinders at least one side of the outer cylinder being coated with a dielectric to form a fixed gap between the cylinders, inclining the cylinders and passing a voltage across the electrodes to effect the atmospheric pressure plasma treatment of a powder. In JP 06-228739 there is provided a means for surface treating a powder by atmospheric-pressure glow discharge by gas floating the powder with a rare gas or mixture of a rare gas and a gaseous reactant. The treatment occurs in a substantially cylindrical vertical positioned reaction vessel at the bottom of which gas is introduced to float the powder and the exit is out of the top of the vessel carried by the gas having been first subjected to and atmospheric-pressure glow discharge at a pressure higher than atmospheric pressure. In US5399832 there is provided a method for treating an organic or inorganic powder or coating same using an organic monomer using atmospheric pressure glow discharge. In WO 97/29156 there is provided a method of treating deagglomerated particles with plasma activated gas to modify the surface of the particles and species.

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[0003] All of the aforementioned prior art relate to the activation of the powder or applications of coatings using gas phase precursors and typically the results suggest low deposition rates and require high residence times to obtain a sufficiently coated surface.

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[0004] The Coating thickness for particles coated by the present process is 1-200nm. Typically the plasma gas used is helium. The generation of a steady-state glow discharge plasma at atmospheric pressure is preferably obtained between adjacent electrodes which may be spaced up to 5 cm apart, dependent on the process gas used. The electrodes being radio frequency energised with an rms potential of 1 to 100 kV, preferably between 4 and 30 kV at 1 to 100 kHz, preferably at 15 to 40 kHz. The voltage used to form the plasma will typically

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be between 4 and 30 kVolts, however the actual value will depend on the chemistry/gas choice and plasma region size between the electrodes

5 [0005] The present inventors have found that by introducing coating forming material directly to a atmospheric plasma process that higher deposition rates of coating onto powder particles can be achieved. The use of direct injection of coating forming material also provides for the use of a wider range of precursor materials, and the coating process is not restricted to gas phase materials or high vapour pressure liquids. The inventors have also found that in the absence of introduced particles that new particles can be synthesized by the
10 same process within the plasma process.

[0006] Thus, according to the present invention there is provided a method for forming a coating on a powder substrate, which method comprises introducing an atomized coating forming material by direct injection and separately introducing a powder to be coated into an
15 atmospheric plasma discharge and/or an ionized gas stream resulting therefrom, and exposing the powder to the atomized precursor.

[0007] It is to be understood that the coating forming material in accordance with the present invention is a precursor material which can be used to make any appropriate coating.
20 including, for example, a material which can be used to grow a film or to chemically modify an existing surface.

[0008] Alternatively by directly introducing an atomized coating forming material or polymer forming precursor into an atmospheric plasma discharge and/or an ionized gas
25 stream resulting therefrom in the absence of introduced powder particles, then particles of reacted precursor are formed.

[0009] The present invention further provides apparatus for forming a coating on a powder,
30 which apparatus comprises means for generating an atmospheric pressure plasma discharge within which, in use, the powder to be coated is introduced, an atomiser for providing an atomised coating-forming material within the plasma discharge, and means for supplying a coating forming material to the atomiser.

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[0010] Any conventional means for generating an atmospheric pressure plasma glow discharge may be used in the present invention, for example atmospheric pressure plasma jet, atmospheric pressure microwave glow discharge and atmospheric pressure glow discharge.

Typically such means will employ a helium diluents and a high frequency (e.g. > 1kHz) power supply to generate a homogeneous glow discharge at atmospheric pressure via a Penning ionisation mechanism, (see for example, Kanazawa et al, J.Phys. D: Appl. Phys. 1988, 21, 838, Okazaki et al, Proc. Jpn. Symp. Plasma Chem. 1989, 2, 95. Kanazawa et al, Nuclear Instruments and Methods in Physical Research 1989, B37/38, 842, and Yokoyama et al., J. Phys. D: Appl. Phys. 1990, 23, 374).

[0011] The coating-forming material may be atomised using any conventional means, for example an ultrasonic nozzle. The atomiser preferably produces a coating-forming material drop size of from 10 to 100µm, more preferably from 10 to 50µm. Suitable atomisers for use in the present invention are ultrasonic nozzles from Sono-Tek Corporation, Milton, New York, USA. The apparatus of the present invention may include a plurality of atomisers, which may be of particular utility, for example, where the apparatus is to be used to form a copolymer coating on a substrate from two different coating-forming materials, where the monomers are immiscible or are in different phases, e.g. the first is a solid and the second is gaseous or liquid.

[0012] The plasma chamber may be orientated vertically, allowing gravity fed processing. For example, if atmospheric pressure glow discharge is employed, using either flat, parallel electrodes, or concentric parallel electrodes, the electrodes may be orientated vertically. In this case powder to be treated is introduced at the top of the plasma chamber and passes through the plasma region, where atomised coating forming material is introduced.

Polymerisation and crosslinking reactions occur within the plasma region to produce powder particle with well adhered coatings. The coated powder particles then exit the chamber at the base. Alternatively, atomized coating forming material or polymer forming precursor may be introduced into the top of the plasma chamber and polymer particles are formed within the chamber and collected at the base. In both cases, particle flow can be controlled and enhanced by the flow of plasma process gas through the chamber

[0013] The present invention may be used to form many different types of coatings. The type of coating which is formed on the powder substrate is determined by the coating-forming material(s) used, and the present method may be used to (co)polymerise coating-forming monomer material(s) onto the substrate surface. The coating-forming material may be organic or inorganic, solid, liquid or gaseous, or mixtures thereof. Suitable organic coating-forming materials include carboxylates, methacrylates, acrylates, styrenes, methacrylonitriles, alkenes and dienes, for example methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, and other alkyl methacrylates, and the corresponding acrylates, including organofunctional methacrylates and acrylates, including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates, and fluoroalkyl (meth)acrylates, methacrylic acid, acrylic acid, fumaric acid and esters, itaconic acid (and esters), maleic anhydride, styrene, α -methylstyrene, halogenated alkenes, for example, vinyl halides, such as vinyl chlorides and vinyl fluorides, and fluorinated alkenes, for example perfluoroalkenes, acrylonitrile, methacrylonitrile, ethylene, propylene, allyl amine, vinylidene halides, butadienes, acrylamide, such as N-isopropylacrylamide, methacrylamide, epoxy compounds, for example glycidoxypropyltrimethoxysilane, glycidol, styrene oxide, butadiene monoxide, ethyleneglycol diglycidylether, glycidyl methacrylate, bisphenol A diglycidylether (and its oligomers), vinylcyclohexene oxide, conducting polymers such as pyrrole and thiophene and their derivatives, and phosphorus-containing compounds, for example dimethylallylphosphonate. Suitable inorganic coating-forming materials include metals and metal oxides, including colloidal metals. Organometallic compounds may also be suitable coating-forming materials, including metal alkoxides such as titanates, tin alkoxides, zirconates and alkoxides of germanium and erbium. However, the present inventors have found that the present invention has particular utility in providing substrates with silica- or siloxane-based coatings using coating-forming compositions comprising silicon-containing materials. Suitable silicon-containing materials for use in the method of the present invention include silanes (for example, silane, alkylsilanes, alkylhalosilanes, alkoxysilanes) and linear (for example, polydimethylsiloxane) and cyclic siloxanes (for example, octamethylcyclotetrasiloxane), including organo-functional linear and cyclic siloxanes (for example, Si-H containing, halo-functional, and haloalkyl-functional linear and cyclic siloxanes, e.g. tetramethylcyclotetrasiloxane and trifluorobutylmethoxycyclotetrasiloxane). A mixture of different silicon-containing

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materials may be used, for example to tailor the physical properties of the substrate coating for a specified need (e.g. thermal properties, optical properties, such as refractive index, and viscoelastic properties).

- 5 [0014] In addition, under oxidising conditions the present method may be used to form an oxygen containing coating on the substrate. For example, silica-based coatings can be formed on the substrate surface from atomised silicon-containing coating-forming materials. Under reducing conditions, the present method may be used to form oxygen free coatings, for example, silicon carbide based coatings may be formed from atomised silicon
10 containing coating forming materials.

- [0015] Plasma generating conditions containing gases other than oxygen may also be employed, for example noble gases, air, hydrogen, nitrogen and ammonia. In a nitrogen containing atmosphere nitrogen can bind to the substrate surface, and in an atmosphere
15 containing both nitrogen and oxygen, nitrates can bind to and/or form on the substrate surface. Such gases may also be used to pre-treat the substrate surface prior to exposure to the coating forming substance. For example oxygen containing plasma treatment of the powder substrate may provide improved adhesion with the applied coating. The oxygen containing plasma being generated by introducing oxygen containing materials to the plasma such as
20 oxygen gas or water. Furthermore, the coating formed on the substrate may be post treated in a range of plasma conditions. For example, siloxane derived coatings may be further oxidised by oxygen containing plasma treatment. The oxygen containing plasma being generated by introducing oxygen containing materials to the plasma such as oxygen gas or water.

- 25 [0016] An advantage of the present invention over the prior art is that both liquid and solid atomised coating-forming materials may be used to form coatings, due to the method of the present invention taking place under conditions of atmospheric pressure. Furthermore the coating-forming materials can be introduced into the plasma discharge or resulting stream in the absence of a carrier gas, i.e. they can be introduced directly by, for example, direct
30 injection, whereby the coating forming materials are injected directly into the plasma.

- [0017] As mentioned above, the present inventors have found particular utility of the present invention for forming silica- and siloxane-based coatings on powders using silicon-

- containing materials. Under oxidising conditions, e.g. an oxygen containing atmosphere, silica-based coatings can be formed on the substrate surface from atomised silicon-containing materials, whereas under non-oxidising conditions a siloxane polymer, e.g. a linear, branched or resinous siloxane polymer, can be formed on the substrate surface from atomisation of a silicon-containing monomer. A siloxane-organic copolymer can be formed on the substrate surface by use of a mixture of organic and silicon-containing monomers. However, the present invention is also useful for forming an organic coating on a substrate, for example a polyacrylic acid or perfluoro-organic coating.
- 10 [0018] The powder substrates to be coated may comprise any material, for example metals, metal oxides, silica, organic powders, including polymeric, dyestuffs, fragrances, flavouring and pharmaceutical powders.
- 15 [0019] Substrates coated by the method of the present invention may have various utilities. For example a silica based coating may give encapsulation and controlled release properties to an organic particle such as a fragrance or dyestuff. An organic polymeric coating upon a metal or metal oxide particle would provide improved compatibility of the particle in organic media, such as a silver conductive particle within an adhesive, or a silica reinforcing particle within an elastomer.
- 20 [0020] In one embodiment of the invention a statically electric charged porous plate or a vibrating sieve may be placed in line with the exit of the powder from the plasma region to collect the resulting powder.
- 25 [0021] The present invention will now be described further on the basis of the following example and drawing.
- 30 [0022] An atmospheric pressure glow discharge was generated by applying RF power of 1 W/cm² to two electrodes adhered to glass plates that enclose a helium/oxygen gas mixture in the ratio of 98/2. Tetramethylcyclotrisiloxane (TMCTS) was supplied to an ultrasonic nozzle at a flow rate of 200 microlitres per minute. TMCTS droplets were discharged from the ultrasonic nozzle above the atmospheric pressure glow discharge. These TMCTS droplets

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pass through the atmospheric pressure glow discharge and form a fine white powder which was collected below the atmospheric pressure glow discharge.

[0023] Fig. 1 shows an Atmospheric Pressure Glow Discharge Apparatus for Powder

5 Treatment in which the following numerals are identified.

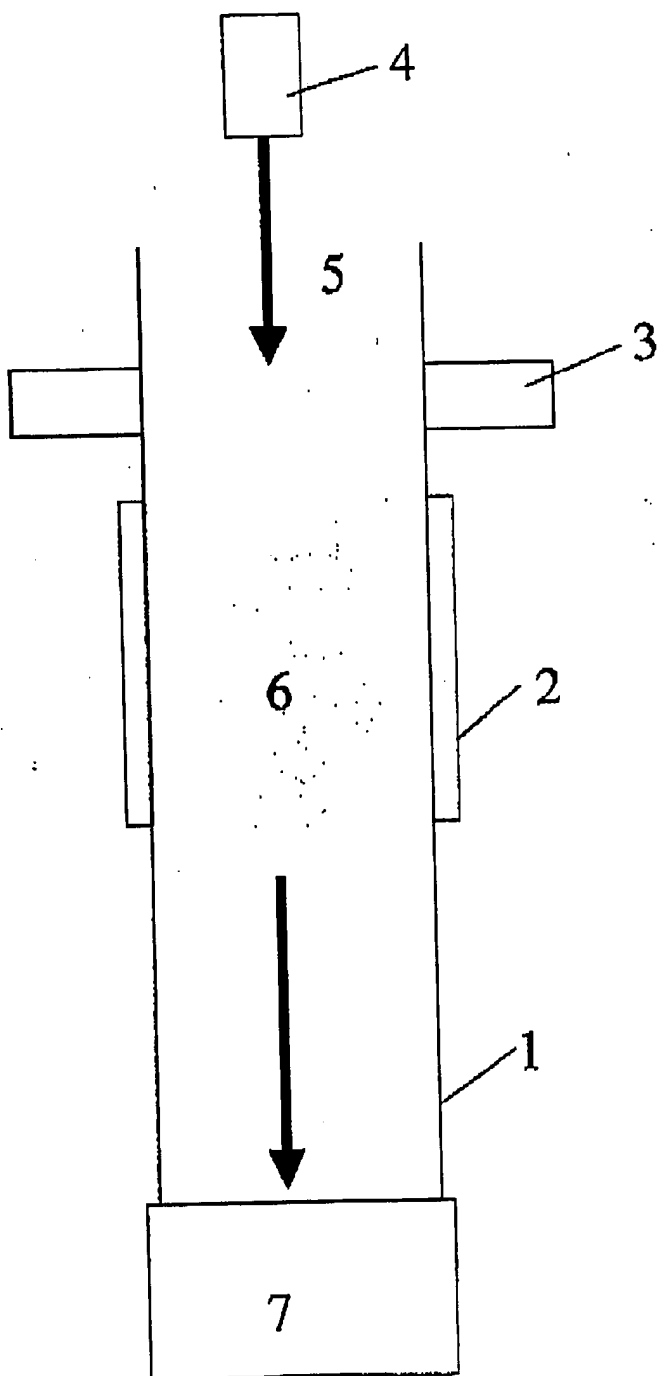
- 1 Dielectric shield
- 2 Parallel electrodes
- 3 Atomiser nozzle
- 4 Powder delivery
- 10 • 5 Powder prior to coating
- 6 Plasma region
- 7 Collector for treated powder

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Claim

1. A method for forming a coating on a powder substrate, which method comprises
introducing an atomized coating forming material by direct injection and separately
5 introducing a powder to be coated into an atmospheric plasma discharge and/or an
ionized gas stream resulting therefrom, and exposing the powder to the atomized
precursor.
2. A method for forming a powder comprising subjecting an atomised liquid to
10 atmospheric plasma and collecting the powder resulting from the plasma treatment.
3. a method in accordance with claim 2 wherein the plasma treatment is atmospheric
pressure glow discharge.
- 15 4. a method in accordance with claim 2 or 3 wherein the atomised liquid was
Tetramethylcyclotetrasiloxane and the resulting powder was silica.
5. an apparatus as hereinbefore described with reference to the drawing.

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